PCT/IB04/50357

Europäisches Patentamt | European Patent Office | Office européen des brevets

REC'D 05 APR 2004
WIPO PCT

05.04.04

Bescheinigung | Certificate | Attestation

Die angehefteten Unterlagen stimmen mit der ursprünglich eingereichten Fassung der auf dem nächsten Blatt bezeichneten europäischen Patentanmeldung überein.

The attached documents are exact copies of the European patent application described on the following page, as originally filed.

Les documents fixés à cette attestation sont conformes à la version initialement déposée de la demande de brevet européen spécifiée à la page suivante.

BEST AVAILABLE COPY

Patentanmeldung Nr. | Patent application No. | Demande de brevet n°

03100879.0

PRIORITY DOCUMENT

SUBMITTED OR TRANSMITTED IN COMPLIANCE WITH RULE 17.1(a) OR (b)

Der Präsident des Europäischen Patentamts; Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets p.o.

R C van Dijk

Anmeldung Nr:
Application no.: 03100879.0
Demande no:

Anmeldetag:
Date of filing: 02.04.03
Date de dépôt:

Anmelder/Applicant(s)/Demandeur(s):

Koninklijke Philips Electronics N.V.
Groenewoudseweg 1
5621 BA Eindhoven
PAYS-BAS

Bezeichnung der Erfindung/Title of the invention/Titre de l'invention:
(Falls die Bezeichnung der Erfindung nicht angegeben ist, siehe Beschreibung.
If no title is shown please refer to the description.
Si aucun titre n'est indiqué se referer à la description.)

Method of manufacturing a flexible electronic device and flexible device

In Anspruch genommene Prioriät(en) / Priority(ies) claimed /Priorité(s) revendiquée(s)
Staat/Tag/Aktenzeichen/State/Date/File no./Pays/Date/Numéro de dépôt:

Internationale Patentklassifikation/International Patent Classification/
Classification internationale des brevets:

H01L21/

Am Anmeldetag benannte Vertragstaaten/Contracting states designated at date of filing/Etats contractants désignées lors du dépôt:

AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IT LU MC NL
PT SE SI SK TR LI RO

Method of manufacturing a flexible electronic device and flexible device

The invention relates to a method of manufacturing a flexible electronic device provided with a substrate having a first and an opposed second side and an electronic element, in which method the substrate is attached to a transparant and rigid carrier with an adhesive layer, therewith resulting in first bonds between the adhesive layer and the substrate and in second bonds between the adhesive layer and the carrier, which adhesive layer is irradiated after some process steps to enable delamination of the substrate from the carrier, therewith obtaining the flexible device.

The invention also relates to a flexible electronic device comprising a substrate having a first and an opposed second side, that is at the second side provided with an electronic element.

Such a method and such a device are known from EP-A 1256983. In the known method use is made of a semiconductor substrate in which transistors are defined. In the particular example given, the semiconductor substrate is a silicon substrate with a buried insulator layer. After attaching the substrate to a temporary carrier with an adhesive layer, the substrate is removed up to the insulator layer. A polyimide coating may be applied thereafter, to protect the transistors. Finally the adhesive layer is irradiated through the transparent carrier, and the substrate as far as left with the stack of layers thereon is delaminated from the carrier.

It is a disadvantage of the known method, that the method relies on a semiconductor substrate. The use of such a substrate is not only expensive, but it also sets limits to the achievable size of the electronic device. Generally, silicon wafers have a diameter of 6 or 8 inch (15 or 20 cm), and if larger, they will be more expensive. Particularly for display applications, however, larger sizes are desired.

It is therefore a first object of the invention to provide a method of the kind mentioned in the opening paragraph, in which the use of a silicon substrate is not required.

It is a second object of the invention to provide a flexible device that can be manufactured with the method of the invention.

The first object is achieved in that the method comprises after lamination the steps of:
applying layers at the second side of the substrate, in which layers the thin-film electronic element is defined, one of the layers being an active layer of semiconductor material, this active layer being protected from the adhesive layer through an opaque coating;
irradiating the adhesive layer through the carrier, therewith weakening the second bonds, and delaminating the substrate from the carrier, therewith obtaining the device.

The method of the invention results in thin-film type electronic elements, instead of the silicon based electronic elements of the prior art. These thin-film type electronic elements are defined only after that the substrate is attached to the carrier. This imposes strict conditions on the behaviour of the adhesive layer; not only has the substrate to be substantially flat, but also is an overlay precision on a micrometer scale required.

In a preferred embodiment, the carrier and the substrate are given after lamination a heat treatment to a temperature of at least a process temperature of any layer to be applied and at most a degradation temperature of the adhesive layer. For many applications the temperature stability of the adhesive layer must be very good; e.g. the original sizes must still be retained after several heating and cooling steps, such are necessary for the patterning and/or the deposition of the layers in which the thin film element is defined. It is not always the case, that the temperature stability is good enough without any additional measures. The heat treatment of this embodiment is such additional measure. As a result thereof, the stack of adhesive layer and substrate will expand or shrink as it will do afterwards. It was found that with such a heat treatment the adhesive layer gets the required temperature stability, and the layers can be applied with an overlay precision in the order of micrometers or less.

The necessity for the overlay precision is particularly present in the case that the electronic element is a transistor, and more particularly for transistors for use in displays. In such transistors, the gate electrode should overlay channel and source-and drain-electrodes as precisely as possible. If the gate electrode is displaced towards the source electrode or in the opposite direction towards the drain electrode, the parasitic capacity between gate and source or drain is increased. This influences the transistor performance and the display quality. A further negative effect is that the variation in transistor performance increases. If the gate electrode is displaced in a direction transversally oriented thereto, a leakage current may result, giving rise to non-functioning of the transistor. The problem is particularly pertinent, since with uncontrolled expansion of the adhesive layer and substrate, the overlay

will be different at the edges of the structure than in the center thereof. Contrarily, these strict conditions are not necessary in the prior art, wherein the carrier is only attached to the substrate after that the transistors have been defined.

Furthermore, the surface of the substrate should be planar before applying any of the functional layers, which generally have a thickness in the submicrometer range. A planarisation layer may be applied on top of the substrate for this reason. However, particularly if the substrate and the adhesive layer are applied together onto the carrier, this is not necessary anyway. Besides, any planarisation layer increases the thickness with the result of reduced flexibility.

The selective weakening of one of the first and the second bonds is necessary, in order that the adhesive layer will not be prone to tear apart during delamination. Such selective weakening generally takes place at the interface between the carrier and the adhesive layer in view of the fact that the intensity of the radiation is the highest at the interface. The adhesive layer will then adhere to the substrate after delamination, and can be used as a mechanical protection layer.

The selective weakening can be improved but also set by various means, for instance surface treatments to strengthen the first bonds and weaken the second bonds. A preferred alternative hereto, is that the adhesive layer comprises dyes. Such dyes will lead thereto that more radiation is received near the interface of carrier and adhesive layer than near the interface of adhesive layer and substrate. A preferred embodiment of a dye is a photosensitive component. The use of the proper photosensitive component has the additional advantage that it also leads to cross-linking in the adhesive layer. With such cross-linking the adhesive layer becomes more rigid, which coincides with less adhesive strength.

The adhesive layer may contain various materials. Preferably it comprises reactive additives that upon illumination with UV radiation lower the glass transition temperature of the primary polymer component in the adhesive layer. Particularly, the additives may lead to cross-linking between polymer chains, therewith forming a polymer network with a reduced glass transition temperature. In the glassy state the adhesion strength of the adhesive layer is considerably reduced, thus enabling easy delamination. The glass transition temperature may be lowered to room temperature. However, if the glass transition temperature after the UV irradiation is above room temperature, for instance at 40 °C, the delamination may be done under gentle heating. A suitable composition for the adhesive layer is known per se from WO-A 02/06413.

As additives, preferably low molecular additives are used. A preferred additive is an (meth)acrylate-type compound. This may for instance be used together with any acrylic acid. Alternatively, such additives may be present in polymeric form.

Preferably, the adhesive layer has a thickness in the range of 5-40 micrometers. Such a limited thickness reduces shear displacements. Hence, the alignment of the various layers is improved, and the overlay precision of the layers can be obtained within the specification of the transistor. Furthermore, if the adhesive layer adheres to the substrate after delamination, a limited thickness of the layer is important in order to provide the required flexibility.

The protective means for the active layer is a reflective layer in particular. Such reflective layer may be present in the substrate. Suitable reflective layers include a stack of silicon nitride and silicon oxide, and metal films. The reflective layer may be a stack of a plurality of sublayers. The reflective layer and the wavelength of radiation to irradiate the adhesive layer can be mutually optimized. An advantage of the reflective layer is that it will protect the thin-film element against degradation through oxygen and water as well. A further advantage of the reflective layer is that the dose of irradiation can be reduced with about 50%. Alternatively or in addition thereto one of the functional layers, such as an electrode layer of Au, acts as protective layer.

In an advantageous embodiment, the thin-film electronic element is a thin-film transistor provided with a source- and a drain-electrode mutually separated through a channel and a metallic gate-electrode separated from the channel through a gate dielectric, wherein the metallic gate-electrode acts as the opaque coating. Such a thin-film transistor has a so-called bottom-gate structure. The gate-electrode, preferably of gold, will herein protect the semiconductor material from the radiation to be used for chemically modifying the adhesive layer or part thereof.

The semiconductor material used in the element of the invention may be any semiconductor material such as amorphous or polycrystalline silicon, zinc sulphide or other inorganic semiconductor material, nanostructures such as nanowires and nanotubes of semiconductor material, including carbon, and organic semiconductors, including herein also organic semiconductor materials used in light-emitting diodes. Particularly preferred is the use of an organic semiconductor material in transistors. Herewith a device can be made that is not just flexible, but even rollable and able to be integrated in paper. Organic semiconductor materials are for instance polyphenylene-vinylenes, polyfluorenes, oligothiophenes, pentacene, fullerene, polyarylamines, polythiophenes, polythienylene-

vinylenes, which materials may be provided with alkyl-, alkoxy-, aryl-aryloxy-side chains or other side chains. Furthermore, such materials may be copolymers and blends, including copolymers of semiconducting oligomers with non-semiconducting monomers.

The adhesive layer can be provided on the substrate before laminating both to the carrier. This is interesting in that the stack of substrate and adhesive layer will be commercially available. However, the adhesive layer and the substrate must be able to withstand the required process temperatures. It may therefore be preferred to provide an optimized adhesive layer by spin-coating. The substrate may thereafter be provided by laminating, but alternatively by spincoating.

The process temperatures used in the application of the further layers. Higher temperatures are for instance necessary to bake photoresists, if any, to convert a precursor material into an organic semiconductor material, if present, to provide the electrically conductive layers, to enable electrical contact between the semiconductor material and the electrodes, and to provide any electro-optical layer. Such electro-optical layer can be provided on top of the transistors, with preferably a protective and/or a planarizing layer in between of the transistor and the electro-optical layer. The required process temperatures are generally in the range of 100 to 200 °C.

The irradiation is preferably radiation of the UV-spectrum, for instance with a wavelength between 250 and 400 nm. It may be provided as a low-intensity, for instance of 1-100 mW, preferably 5-40 mW, so as to prevent negative impact on any of the functional layers in the device.

The second object is achieved in a flexible electronic device comprising a substrate having a first and an opposed second side, that is at the first side provided with an adhesive layer having a surface substantially without adhesive strength, and is at the second side provided with a thin-film electronic element. This flexible electronic device results when the second bonds are weakened and the device is delaminated from the carrier with the adhesive layer adhered to the substrate.

The electronic element is preferably a transistor. More preferably a plurality of transistors and an electro-optical layer are present, therewith constituting a display, at least part of which transistors functioning as pixel transistors of the display. As the manufacture of the electronic element is not limited to the size of a semiconductor wafer, very large flexible displays, with 12, 15 or 20 inch diameter, can be realized. Such transistors may

include an organic semiconductor material, which allows the manufacture of rollable displays.

The adhesive layer suitable comprises a polymer network. Such polymer network will have developed as a consequence of irradiation, if certain compounds are present. It is advantageous in that herewith the adhesive layer - and thus the device - is provided with a somewhat more rigid surface. Such surface is less prone to mechanical damage.

These and other aspects of the invention will further be explained with reference to the figures, which are purely diagrammatical and not drawn to scale, and in which the same reference numbers refer to the same or equivalent parts, and in which:

Fig. 1A-D shows cross-sectional views of several stages in the method of the invention.

Fig. 1A shows a transparent and rigid carrier 20, which is made of glass in a thickness of 1 cm. Its surface is well cleaned in conventional manner. The figure further shows a substrate 1 with a first side 11 and a second side 12. The substrate 1 is at its second side 12 provided with an adhesive layer 15. The substrate 1 and the adhesive layer 15 are provided in a roll and per se commercially available, from Ultron, or from Teijin (type DT120 B60). The substrate 1 comprises for instance polyvinylchloride or polyethyleneterephtalate (PET) or polyimide, and had in one example a thickness of 120 micrometer. The adhesive layer 15 comprises for instance a copolymer of acrylic acids and has a thickness of 15 micrometer. Dialkylphtalate was present as a plasticizer in the adhesive layer. It further comprises a photoinitiator, which acts as dye as well. Suitable examples of photoinitiators include benzophenone, 4,4'-bis(dimethylamino)benzophenone, 2-ethylanthraquinone and benzoin ethers. Suitable photoinitiators and suitable adhesives are known per se from US5,455,142, which is herein included by reference. In between of the substrate 1 and the adhesive layer 15 reflective layer of Al can be provided in a suitable thickness of 100-300 nm.

Fig. 1B shows the carrier 20 and the substrate 1 after adhesion of the adhesive layer 15 on the carrier 20. Herewith second bonds between the adhesive layer 15 and the carrier 20 have been formed. The combination of a glass carrier and a hydroxyl-groups containing adhesive, such as an acrylate-based adhesive, is herein advantageous in that the hydroxylgroups can form bonds with the glass network easily. First bonds between the

adhesive layer 15 and the substrate 1 had been formed before. However, this is certainly not essential. After this adhesion, a heat treatment is done at 180 °C for about 30 minutes, and is thereafter cooled to room temperature quietly. Hereafter, the substrate 1 is given a oxid plasma treatment to make its first side 11 hydrophilic, after which a suitable planarisation layer is provided, for instance a photoresist layer like SU8, HPR504, or benzocyclobutene, SiLK, polyvinylphenol. In this case, a solution of polyvinylphenol (Polysciences Inc, cat 6527) and hexamethoxymetylenemelamine (Cymel 300 from Cyanamid) in propylene glycol methyl ether acetate (Aldrich) was spincoated (3s/500 rpm, 27s/2000 rpm) and then dried at 110 °C for 1 min on a hotplate. Cross-linking at 125 °C in a nitrogen atmosphere containing 5% v/v HCl for 5 min affords a 1.5 micron thick cross-linked polyvinylphenol film.

Fig. 1C shows the result after the functional layers of the electronic components have been provided. In this case the electronic elements are transistors, which are used as pixel transistors for driving a display. A suitable electro-optical layer is an electrophoretic layer containing micro-capsules, such as known per se from US6,262,833. The display comprises a plurality of pixels and pixel electrodes, for instance 400, and arranged in a matrix, to drive them according to active matrix principles, such as known from WO02/71137.

The transistor comprises a source electrode 21, a drain electrode 22, which electrodes are mutually separated through a channel 23 and are defined in a first electrode layer of electrically conductive material 2. The source-electrode 21 is connected to the pixel electrode 29. A second electrode layer 3 of electrically conductive material is present at this side 11 of the substrate 1 as well. A gate electrode 24 has been defined in this second electrode layer 3. A perpendicular projection of this gate electrode 24 on the first electrode layer 2 shows a substantial overlap with the channel 23. Furthermore, an intermediate layer 4 of dielectric material and an active layer 5 comprising a semiconductor material are present.

Said layers 2,3,4 and 5 are present on the substrate 1 in the order of second electrode layer 3, intermediate layer 4, first electrode layer 2 and active layer 5. The second electrode layer 3 comprises Au and has been patterned photolithographically in conventional manner with a photosensitive resist material. The photoresist material was after irradiation heated to about 120 °C and afterwards wet-chemically etched. A non-shown monolayer of $CH_3-(CH_2)_{15}-SH$ may be applied between the second electrode layer 3 and the intermediate layer 4 to prevent the existence of pinholes in the intermediate layer 4. The intermediate layer 4 comprises an organic dielectric that can be structured photochemically, such as for instance benzocyclobutene, polyimide, polyvinylfenol or a photoresist, and in this case the

commercially available photoresist material HPR504. It has a thickness in the order of 200-500 nm and is provided with contact holes so as to provide vertical interconnects from the first to the second electrode layer 2,3. The first electrode layer 2 comprises gold in this case and is provided with sputtering and in conventional manner structured photolithographically. Alternatively, it may contain a polymeric conductor, such as poly(3,4-ethylene)dioxythiophene (PEDOT) together with a polyacid. Such polymeric conductor can be structured by adding a photo-initiator, such as described in WO-A 01/20691, while the conductivity is maintained. The first or the second electrode layer 2,3 further comprises (non-shown) contacts for external contacting, as well as interconnect lines. The active layer 5 comprising pentacene and polystyrene (99 to 1 % by weight), wherein the polystyrene acts as carrier material. The pentacene was converted from precursor pentacene having a tetrachlorocyclohexadiene leaving group after application as active layer on the substrate. The conversion took place at 180 °C for three minutes. On the active layer 5 a protective layer 6 of electrically insulating material is present, as well as a photoresist 7. The layers 5, 6 and 7 form a stack and are provided with one and the same pattern.

Hereafter an electro-optical layer 8 is provided. This layer may be provided in by printing or coating. It comprises a contrast media phase, which preferably is an encapsulated electrophoretic phase, and further known from US6,262,833. It further comprising a polymeric binding phase. Such binding phase is preferably water-soluble and chosen from the group of polysaccharides, polyvinylalcohols, poly-hydroxyalkylacrylates, polyacrylates, polyesters and polycarbonates. After application of the layer it is dried at 60-80 °C for about 30 minutes. On top of the electo-optical layer 8 a third electrode layer 9 is provided. The third electrode layer comprises transparent electrodes and is made of Indium Tin Oxide, or preferably of a polymeric conductor, such as PEDOT.

Fig. 1D shows the resulting flexible device 10, after that the carrier 20 has been delaminated from the substrate 1. Hereto, the adhesive layer 15 is irradiated through the substrate with UV-radiation of 250-400 nm at an intensity of 10 mW during 30 minutes. As a result of the second electrode layer 3 acting as protective layer no negative impact on the active layer 5 has been found to occur. After the irradiation, which is presumed to result in cross-linking the adhesive layer 15 has lost substantially its adhesive strength.

Example 1

An adhesive is prepared on the basis of ethyl lactate, in which are present 20 wt% Poly(vinyl acetate-co-crotonic acid), 30 wt% dipentaerythritol penta/hexa acrylate, 4.5 wt% 2-hydroxyethyl acrylate, 0.3wt% Irgacure 651. This adhesive is spin coated on a glass substrate (3s 500rpm + 30s 1000rpm) and dried at 90°C for 3 minutes on a hot plate. After this a 30μm polyimide foil is laminated at room temperature. The stack is heated to 200°C in a convection oven followed by slow cooling to 100°C. After this layers are provided to obtain a transistor, as explained above with reference to the figure 1C. Use is made of gold for the first and the second electrode layers 2,3. The mis-alignment of the first and second gold layer is within the specification (< 2.5μm). Subsequently the adhesion strength of the adhesive can be reduced by illuminating the adhesive through the glass substrate (dose 300 mJ/cm² @ 365 nm). The transistor stack is then removed from the underlying glass substrate.

CLAIMS:

1. A method of manufacturing a flexible electronic device provided with a substrate having a first and an opposed second side and a thin-film electronic element, which method comprises the steps of:

- attaching the substrate with its first side to a transparent and rigid carrier with an adhesive layer, therewith resulting in a stack of carrier, adhesive layer and substrate with first bonds between the adhesive layer and the substrate and with second bonds between the adhesive layer and the carrier;
- applying layers at the second side of the substrate, in which layers the thin-film electronic element is defined, one of the layers being an active layer of semiconductor material, this active layer being protected from the adhesive layer through an opaque coating;
- irradiating the adhesive layer through the carrier, therewith weakening one of the first and the second bonds, and
- delaminating the substrate from the carrier, therewith obtaining the device.

2. A method as claimed in Claim 1, wherein a heat treatment is given to the carrier and substrate after lamination, in which heat treatment the temperature is increased to a temperature of at least a process temperature of any layer to be applied and at most a degradation temperature of the adhesive layer.

3. A method as claimed in Claim 1, wherein the second bonds are weakened selectively, therewith obtaining the device with the adhesive layer adhered to the substrate.

4. A method as claimed in Claim 1 or 3, wherein the adhesive layers comprises at least one dye.

5. A method as claimed in Claim 1, wherein the adhesive layer comprises a main polymeric component and an UV-sensitive reactive additive, which upon illumination with UV radiation will lower the glass transition temperature of the polymeric component.

6. A method as claimed in Claim 1, wherein the thin-film electronic element is a thin-film transistor provided with a source- and a drain-electrode mutually separated through a channel and a metallic gate-electrode separated from the channel through a gate dielectric, wherein the metallic gate-electrode acts as the opaque coating.

7. A flexible electronic device comprising a substrate having a first and an opposed second side, that is at the first side provided with an adhesive layer having a surface substantially without adhesive strength, and is at the second side provided with a thin-film electronic element.

8. A flexible electronic device as claimed in Claim 7, wherein the electronic element is a transistor.

9. A flexible electronic device as claimed in Claim 8, wherein the transistor comprises an organic semiconductor material.

10. A flexible electronic device as claimed in Claim 8 or 9, wherein a plurality of transistors and an electro-optical layer are present, therewith constituting a display, at least part of which transistors functioning as pixel transistors of the display.

ABSTRACT:

An electrical element, such as a thin-film transistor, is defined on a flexible substrate, in that the substrate is attached to a carrier with an adhesive layer, and is delaminated after definition of the transistor due to illumination by UV-radiation. An opaque coating is provided to protect any semiconductor material. A heat treatment is preferably given before application of the layers of the transistor to reduce stress in the adhesive layer.

Fig. 1D

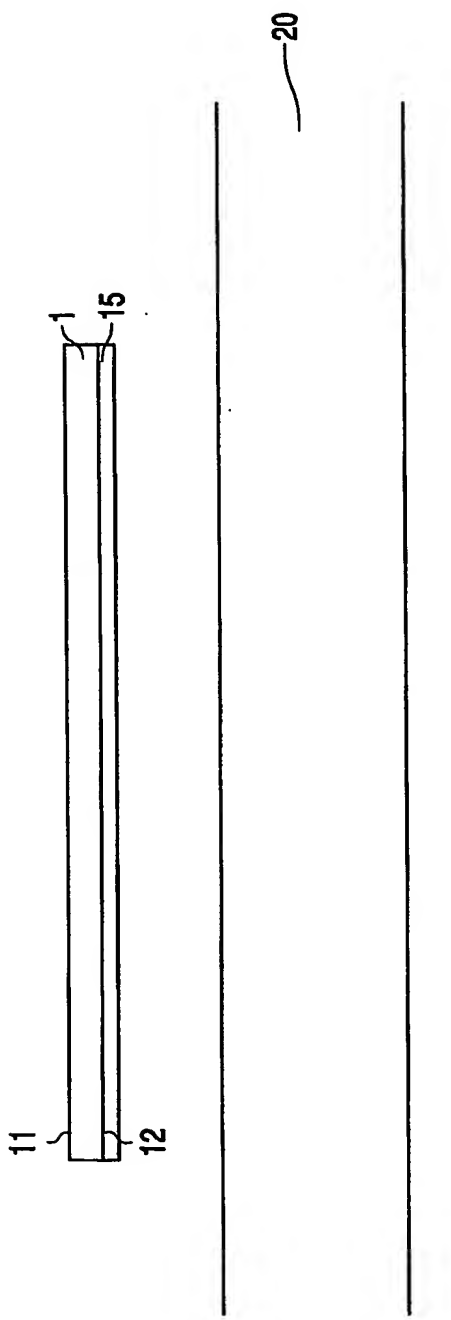


FIG. 1A

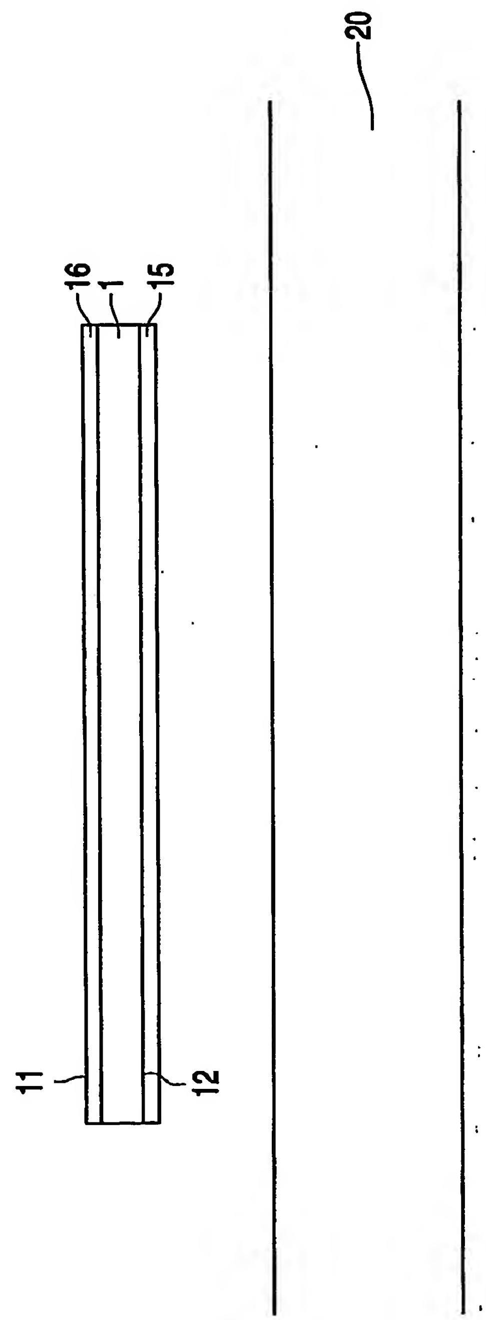


FIG. 1B

FIG. 1C

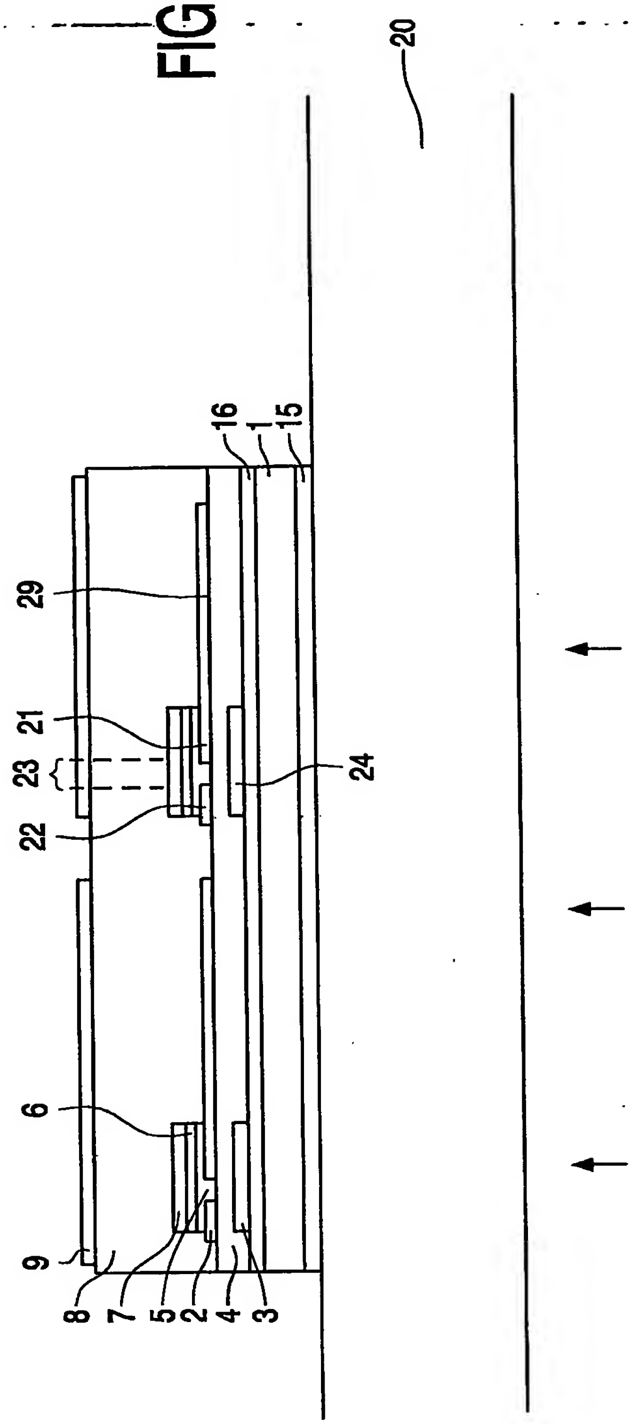
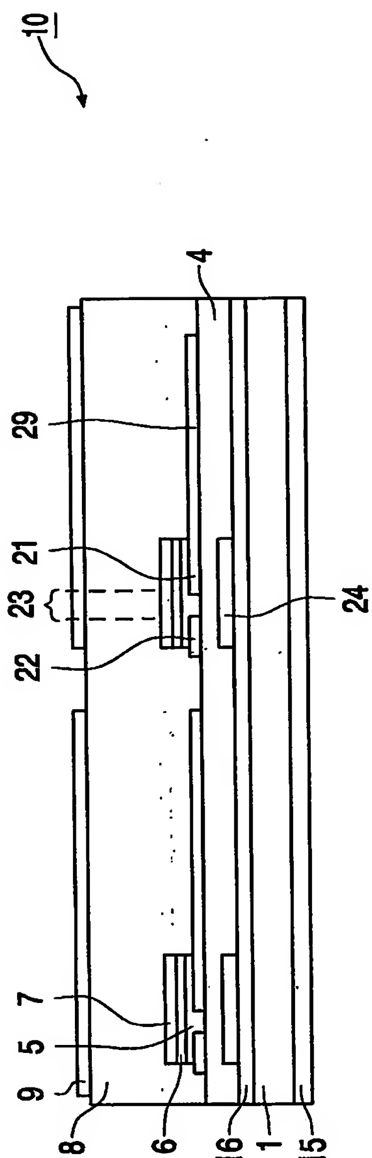


FIG. 1D



PCT/IB2004/050357